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XVI МІЖНАРОДНА КОНФЕРЕНЦІЯ З ФІЗИКИ І ТЕХНОЛОГІЇ
ТОНКИХ ПЛІВОК ТА НАНОСИСТЕМ

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**XVI INTERNATIONAL CONFERENCE ON PHYSICS AND
TECHNOLOGY OF THIN FILMS AND NANOSYSTEMS**

(dedicated to memory Professor Dmytro Freik)

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Structural and Optical Features of $\text{Cu}_2\text{ZnSnS}_4$ Films Deposited by Pulsed Spray Pyrolysis Technique

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The quaternary compound semiconductor $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) is a perspective material for the absorber layers in 3rd generation thin film solar cells. CZTS has *p*-type conductivity, high absorption coefficients ($\alpha > 10^4 \text{ cm}^{-1}$), as well as band gap ($E_g = 1.0\text{-}1.5 \text{ eV}$) close to Shockley-Queisser efficiency limit (32-34 %). The solar cells based on CZTS absorber layer showed the maximum efficiency of 12.6 %, but this value is significantly lower than ones demonstrated by other thin film solar cells with traditional CdTe (22.1 %) and CIGS (22.3 %) absorbers. This is due to CZTS films have the suboptimal structural characteristics and stoichiometry, secondary phases with different band gaps, the coexistence of kesterite and stannite phases with low transformation energy (3-4 meV/atom).

A range of applications (first of all in photovoltaics and thermoelectrics) require CZTS films deposited onto substrates with large surface area, including flexible ones. It could be achieved by applying the chemical pulsed spray pyrolysis technique which is non-vacuum, low-cost and versatile method allowing deposition of the different semiconductor materials at the moderate temperatures. One of the most important parameter of films is a thickness that could be varied by changing the volume of sprayed solution. The specified above determined the goal of work – the investigation of morphological, structural, optical properties and elemental composition of CZTS thin films obtained by pulsed spray pyrolysis at a different volume of sprayed initial precursor.

$\text{Cu}_2\text{ZnSnS}_4$ films were obtained at $T_s = 673 \pm 10 \text{ K}$ using a water-based precursor contained $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, ZnCl_2 , $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, NH_2CHNH_2 onto glass substrates. The volume of sprayed solution was set in the range of (2-5) ml with $\Delta = 1 \text{ ml}$. The main deposition parameters were used as follows: distance between the nozzle and substrate surface – 20 cm, carrier gas – 0.2 MPa, spraying velocity – 3 ml/min, the time between two spraying cycles – 10 s.

It was determined that the parameters of crystal lattice were changed in the range of $a = (0.5423\text{-}0.5480) \text{ nm}$, $c = (1.0823\text{-}1.1182) \text{ nm}$, $c/2a = (0.9970\text{-}1.0203) \text{ nm}$, volume of unit cell – $(0.3183\text{-}0.3358) \text{ nm}^3$. The chemical composition of films was varying for Cu = (26.43-28.56) at.%, Zn = (15.18-21.36) at.%, Sn = (14.33-15.39) at.% and S = (35.75-43.00) at.%. The samples, deposited in optimal conditions, had the almost single structure of kesterite, as well as stoichiometry and band gap, which are close to the optimal values for designing highly efficient solar cells. The research results can be applied in the development of 3rd generation thin film SC.